Bioresource Technology 155 (2014) 15–20

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Dominant thermogravimetric signatures of lignin in cashew shell as compared to cashew shell cake

Sandip Gangil *

Agricultural Energy and Power Division, Central Institute of Agricultural Engineering, Bhopal, MP, India

HIGHLIGHTS

- Cashew shell and cashew shell cake were proved as different bio-materials.
- Cashew shell had dominant thermogravimetric signatures of lignin.
- Activation energy of lignin was less in cashew shell cake than in cashew shell.
- Activation energy profile of cashew shell dominates over cashew shell cake.

ARTICLE INFO

Article history:
Received 6 November 2013
Received in revised form 16 December 2013
Accepted 18 December 2013
Available online 27 December 2013

Keywords:
Kinetics
Thermogravimetry
Activation energy
Cashew shell cake
Cashew shell

ABSTRACT

Dominant thermogravimetric signatures related to lignin were observed in cashew shell as compared to these signatures in cashew shell cake. The phenomenon of weakening of lignin from cashew shell to cashew shell cake was explained on the basis of changes in the activation energies. The pertinent temperature regimes responsible for the release of different constituents of both the bio-materials were identified and compared. The activation energies of cashew shell and cashew shell cake were compared using Kissinger–Akahira–Sunose method. Thermogravimetric profiling of cashew shell and cashew shell cake indicated that these were different kinds of bio-materials.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Cashew (*Anacardium Occidentale*) (Nair, 2010) is one of the important horticultural evergreen tropical cash crops. Cashew nut is used for human consumption whereas the remaining part, its shell, is utilized for oil and energy generation. This approach uses this biomass resource, completely, by avoiding any kind of wastage of biomass produced. Cashew shell (CS) is the by-product of cashew industry (Tippayawong et al., 2011; Singh, et al., 2006). Cashew nut is covered by a shell of about 2–3 mm thickness. Inside this shell, cashew shell contains a dark reddish brown viscous liquid which is called cashew nut shell liquid (CNSL) (Kasiraman et al., 2012; Das and Ganesh, 2003; Das et al., 2004), and CNSL has commercial value. Cashew nut shell liquid is extracted from the cashew shell. The material left after the extraction of CNSL from cashew shell is cashew shell cake. According to Patel et al. (2006), there are various methods for the extraction of CNSL from CS, which include, open pan roasting, drum roasting, hot oil roasting, cold extrusion, solvent extraction, etc. In Africa, the CNSL present in CS is 15–20% by weight of the unshelled nut, and in India, it is about 25–30% by weight (Patel et al., 2006; Das and Ganesh, 2003). During the process of CNSL-extraction, some amount of CNSL may remain on the surface of cashew shell cake. Further, the configuration of lignin present in CS is affected during the CNSL – extraction process. The temperature and pressure are the critical parameters in the CNSL – extraction process (Patel et al., 2006). The parameters of CNSL – extraction process changes inner bio-matrix of cashew shell during its conversion to cashew shell cake. These changes can be understood using the thermogravimetry.

Thermogravimetry is a tool to understand the thermal decomposition behavior of a bio-material when subjected to heat in precisely monitored chamber. The decomposition of different components of bio-material can be identified for any specific bio-material. According to Vasile et al. (2011), at low heating rates less than 100 °C/min, the thermal decomposition of bio-materials can be described in the stages of moisture removal, hemicellulose decomposition, cellulose decomposition and lignin decomposition.

---

* Address: Agricultural Energy and Power Division, Central Institute of Agricultural Engineering, Bhopal 462038, MP, India. Tel.: +91 755 2521132, +91 9754913685; fax: +91 755 2734016.

E-mail address: gangilsandip@yahoo.co.in

0960-8524/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.12.087

López-González et al. (2013) stated that lignin is the most thermally stable component. Based on thermogravimetric results, the activation energies for different constituents evolved during thermal decomposition process can be estimated. The comparison of two or more bio-materials can be done and the prominence of some specific constituent in a particular bio-material can be established. Kinetics of biomass degradation were critically reviewed and analyzed by White et al. (2011) and Damartzis et al. (2011). The activation energy for thermal decomposition can be obtained using different models and methods (Abdullah et al., 2010; Damartzis et al., 2011; Ledakowicz and Stolarek, 2002; Lu et al., 2009; Sait et al., 2012; Vasile et al., 2011; Wang et al., 2012; White et al., 2011; Yuliana et al., 2012). The Coats–Redfern method, Friedman method, Kissinger–Akahira–Sunose (KAS) method and Ozawa–Flynn–wall method are some of the most commonly used methods for determination of kinetics by the researchers. Basically, all these kinetic models follow Arrhenius equation (Vasile et al., 2011).

Das and Ganesh (2003) and Das et al. (2004), characterized the cashew shell (CS) using FTIR and NMR. Yuliana et al. (2012), stated about the isolation and characterization of the defatted cashew shell starch. They also mentioned about the thermogravimetry for defatted cashew nut shell starch at a single heating rate. Tsamba et al. (2006), (2007), studied the kinetics of coconut and cashew nut shells and also compared activation energies results of different materials quoted by different authors. They mentioned that cashew shells are different than ordinary woody biomass being rich in hydrocarbons. However, the thermogravimetry of CSC was not covered by them. The present writing concentrates on the comparison of the thermal decomposition kinetics of cashew shell cake and cashew shell. We claim that CS is a different bio-material than CSC. The lignin (Carrier et al., 2011; Ciobanu et al., 2004; Pandey and Kim, 2011; Shen et al., 2010) reflected its own dominating thermogravimetric signature in case of cashew shell. The activation energies, of thermal decomposition of CSC and CS, obtained using KAS method are described in this paper. The findings of the kinetic analysis are also important for designing the energy systems for the utilization of CSC and CS. Further, the optimization techniques for the lignin extraction process require the in-depth knowhow of the lignin related thermogravimetric signatures.

2. Methods

For thermo gravimetric analysis, cashew shell cake and cashew shell were powdered using a hammer mill. Powdery bio-material was used for thermal decomposition studies in thermogravimetric analyzer (Model: pyris-6; Make: Perkin Elmer). The heating method used was to keep the system temperature at 30 °C for two minutes and then to raise the temperature at different heating rates from 30 °C to 1000 °C. The inert (Argon) environment was maintained throughout the thermal decomposition of the both types of material. The experimental domain used the heating rates (β) as 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 °C/minute for both the bio-materials. Therefore, a wide range of the heating rates was used to analyze the kinetics. This gives the better estimates of activation energy to design the energy systems. To identify the difference between CS and CSC, the thermogram of both bio-materials were obtained and compared. Thermogravimetry gives the variation of weight loss (%) with respect to temperature or time during thermal decomposition process, and this plot is called "thermogram". The first order derivative of thermogram (decomposition rate profile) is a plot of the weight loss rate (decomposition rate, %. min^{-1}) *versus* temperature or time.

The kinetics was analyzed using the Kissinger–Akahira–Sunose (KAS) method (White et al., 2011; Damartzis et al., 2011) which is an integral iso-conversional method. During the heating of the bio-material at a constant heating rate in inert atmosphere in thermogravimetry, the rate constant of first order reaction depends on temperature according to the Arrhenius equation, $k = A^{*}e^{(-E/RT)}$; where the k is the rate constant, the A is the pre-exponential factor, the E is the activation energy, the R is the universal gas constant and the T is the reaction temperature (absolute). The kinetic parameters can be computed using the following equation (Damartzis, et al., 2011; Doğana, et al., 2008; Sbirrazzuoli, et al. 2009; Shukla, et al., 2010; White, et al., 2011; Ledakowicz and Stolarek, 2002);

$$\ln\left[\frac{\beta}{T^2}\right] = \ln\left[\frac{RA}{E}\right] - \ln g(\alpha) - \frac{E}{RT}$$

where $g(\alpha) = \frac{A}{\beta}\int_{T_i}^{T} e^{(-E/RT)}dT$; α, Conversion fraction; $\alpha = (\mathrm{wi} - \mathrm{wt})/(\mathrm{wi} - \mathrm{w}\infty)$; where the wi, wt and w∞ are the masses of bio-material at initial, instantaneous and final stages of decomposition, respectively; A, Pre-exponential factor; R, Universal gas constant; E, Activation energy; T, Reaction temperature (absolute); Ti, Initial absolute temperature; β, Heating rate.

The determination of kinetic parameters in respect of different constituents of a bio-material is possible by slope and intercept of the linear plot of $\ln(\beta/T^2_{\max})$ *versus* $1/T_{\max}$ (Ledakowicz and Stolarek, 2002). For this, the decomposition rate profile is to be deconvoluted in different peaks (segments) related with different constituents of bio-material because devolatilization curve is usually obtained as a sum of the corresponding individual components contributions as stated by López-González et al. (2013). In each segments (peaks), the evolution of each constituent can be considered as a single first order independent parallel reaction (Ledakowicz and Stolarek, 2002). The time derivative of decomposition rate becomes zero at the peak temperature ($T_{\max}$) of each peak where the rate of volatile evolution (decomposition rate) gains the maximum value (Ledakowicz and Stolarek, 2002). Different values of the $T_{\max}$ can be obtained for each volatile segment (peak) by thermogravimetric profiling at different heating rate (β). In KAS method, the iso-conversional lines can also be used to find the kinetics with respect to the conversion fraction of the bio-material (Damartzis, et al., 2011; Doğana, et al., 2008; Sbirrazzuoli, et al. 2009; Shukla, et al., 2010; White, et al., 2011) wherein we can find linear kinetic plot between $\ln(\beta/T^2)$ *versus* $1/T$ at a specified conversion fraction. Slopes of these linear lines are the measures of $-$E/R at specified conversion fractions.

3. Results and discussion

3.1. Elemental characterization

The nitrogen, carbon, sulfur and hydrogen contents in cashew shell and cashew shell cake are given in Table 1. Cashew shell has low nitrogen content showing it as the fuel producing the syngas with low level of ammonia during the thermal gasification. Ammonia is responsible for corrosion of the syngas reactor's material and therefore, the use of cashew shell for gasification may enhance the life of reactor. As the sulfur content in CSC was lower than CS, CSC can be considered less toxic fuel. Carbon content in CSC was lower because of the extraction of CNSL from the CS. Ash content (using ASTMD-3174 method) of CSC (2.2%) was lower than the ash content of cashew shell (3.0%) indicating that cashew shell cake has better possibilities of thermal gasification to generate the syngas as compared to cashew shell. The CSC used for the experiments was having true density of 1.12 g/cc at a moisture content of 7.5% and was having ash content of 2.2%. The bulk density of CSC was 0.45 g/cc.

Table 1
Elemental characterization of CSC and CS.

Elements (%)	Cashew shell cake	Cashew shell
Carbon	45.8	55.8
Hydrogen	6.3	6.2
Nitrogen	0.7	0.5
Sulfur	0.4	1.1

3.2. Identification of thermogravimetric signatures of lignin and other constituents

As discussed earlier, extraction of CNSL from CS imparts the changes in bio-matrix of CS. Thus, the changes obtained in the thermogravimetry of CSC in comparison with thermogravimetry of CS indicate about the effect of CNSL-extraction process on the different constituents of CS. Fig. 1 shows first order derivatives of the thermogram of cashew shell and cashew shell cake at a heating rate (β) of 10 °C/min. Fig. 1 clearly indicates that there is a peak at 446.7 °C in the plot related to CS whereas this peak subsides in CSC-plot. This dominating peak in CS was ascribed to lignin (Burhenne et al., 2013; Carrier et al., 2011; Chen and Kuo, 2011; Faravelli et al., 2010; Ledakowicz and Stolarek, 2002; López-González et al., 2013; Vasile et al., 2011). This peak was noticed in all thermogram of CS, obtained at all experimented heating rates.

There were several other lumps in both the plots in Fig. 1 which could not be identified by visible inspection. Therefore, to analyze the differences between the CSC and CS, the decomposition rate plots at all β were deconvoluted in different peaks to find exact location of the thermal decomposition of a particular constituent (Burhenne et al. 2013; Huang et al., 2011; Ledakowicz and Stolarek, 2002; López-González et al., 2013). The Gaussian deconvolution was performed using the PeakFit (version 4.12) program of Sigma plot, for identifying different peaks existing in first-order derivative of each thermogram. The analysis was done with linear baseline with a tolerance of 3%, and a confidence level of 99%. Iterations were repeated till the coefficient of determination for the peak fitting became constant and reached to a value more than 0.99. For all heating rates this condition could be obtained by fitting the five peaks. A typical representation of peak fitting is given for CSC and CS at β (10 °C/min) in Fig. 2 and Fig. 3, respectively.

The comparison of Gaussian deconvoluted peaks of CS and CSC at β (10 °C/min) clearly showed that the lignin related peak was dominating in CS as compared to CSC. The identification of other constituents using deconvoluted peaks is summarized in Table 2. The peak near to 237–238 °C in both the bio-materials was related to hemicellulose (Chen and Kuo, 2011; Shen et al., 2010). A peak which did not figure in CSC and existed in CS at 281.6 °C emerged due to presence of CNSL inside the CS matrix. A peak centering 131.6 °C was found in CSC which was not present in CS. This peak was due to the residual surface CNSL in CSC after the CNSL-extraction process. Both bio-materials showed two peaks related to the cellulose (Vasile et al., 2011; Ledakowicz and Stolarek, 2002; Antal and Varhegyi, 1995). Vasile et al. (2011) stated that in thermal decomposition of cellulose, hydrolysis, oxidation and dehydration processes are side reactions and therefore, the step corresponding to cellulose decomposition may be divided in two other steps, depending on the sample's nature. According to them, cellulose followed two competitive reactions which are depolymerization of residual cellulose followed by the volatilization of levoglucosan (Vasile et al., 2011). The same explanations were agreed in present study, for observing two cellulose related peaks. The locations of cellulose related peaks in our study were almost similar in case of both the bio-materials (CS and CSC). The Ist cellulose peak was at 298.3 and 298.1 °C for CS and CSC, respectively. Position of IInd cellulose peak was 335.7 and 335.4 °C in case of CS and CSC, respectively. The lignin related peak centered at 446.7 °C in CS which weakened in CSC at 418 °C. Both peaks of cellulose in CS plot shifted marginally towards lower temperature in CSC. The Ist and IInd peaks related to cellulose shifted by 0.2 and 0.3 °C, respectively in CSC. The remarkable shift of 28.7 °C in the lignin related peak towards low temperature was observed which showed the weakening of lignin in CSC. It indicated that the major influence of the CNSL-extraction process was on the lignin related peak. Lignin molecules weaken during the CNSL-extraction process due to

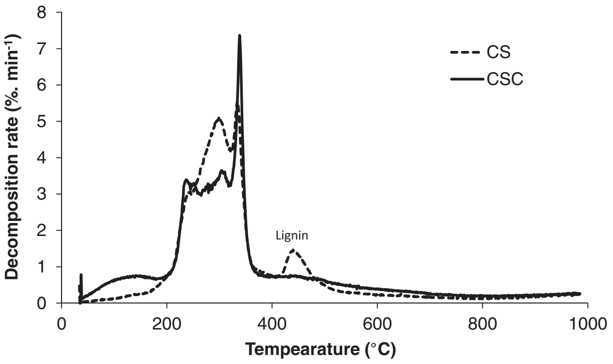

Fig. 1. Comparison of the first order derivative of thermogram of CS and CSC showing the dominant peak of lignin in case of CS.

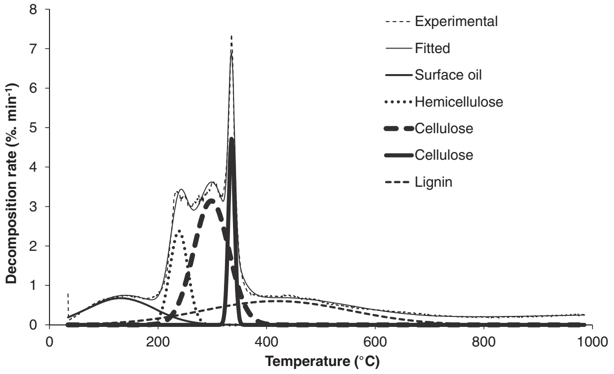

Fig. 2. Gaussian deconvolution of first derivative of thermogram (at 10 °C/min) of CSC.

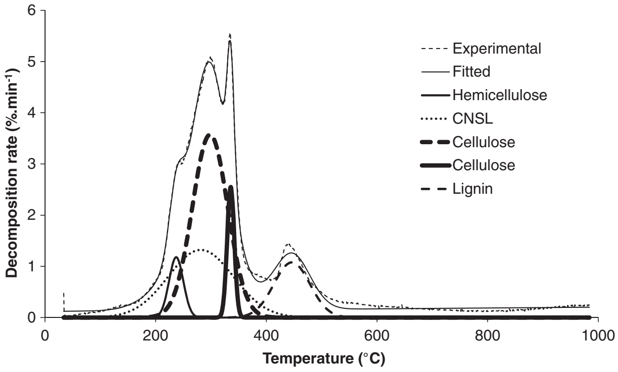

Fig. 3. Gaussian deconvolution of first derivative of thermogram (at 10 °C/min) of CS.

Table 2
Comparison of Gaussian deconvolution of the decomposition rate profiles of CS and CSC at β of 10 °C/min.

Cashew shell	Cashew shell cake	Identification of constituent
–	131.6 (Peak-1)	Surface CNSL and moisture
237.1 (Peak-1)	238.4 (Peak-2)	Hemicellulose
281.6 (Peak-2)	–	Intrinsic CNSL
298.3 (Peak-3)	298.1 (Peak-3)	Cellulose-Ist peak
335.7 (Peak-4)	335.4 (Peak-4)	Cellulose-IInd peak
446.3 (Peak-5)	418.0 (Peak-5)	Lignin

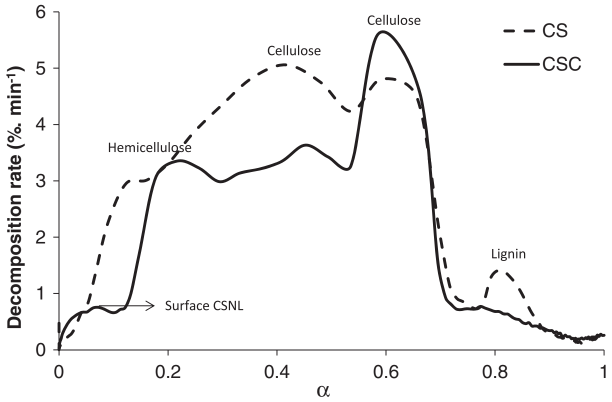

Fig. 4. Decomposition rate *versus* α plots for CS and CSC at β of 10 °C/min.

melting and relaxation. Therefore, the lignin did not prominently reflect in thermogravimetry of CSC. Guigo et al. (2009) studied molecular mobility and relaxation process of isolated lignin and mentioned that the relaxation process of annealed lignin showed a different behavior as the consequence of micro-structural modifications of lignin. These modifications were explained by Guigo et al. (2009) as the redistribution of secondary bonds as well as formation of new interunit linkages. During the CNSL-extraction process, CS undergoes through stresses due to temperature or pressure or both, creating some sort of annealing effects. Present article considered that combined effects of the breaking of bonds, within lignin, and between lignin and other components, were responsible for "weakening of lignin". Relaxation was associated with the breaking of bond within lignin whereas the melting was related to breaking of bonds of lignin with other components. As thermogravimetric signatures of lignin in CS were at higher temperature locations than in CSC, lignin needed higher energy for its own activation. That is why; higher activation energy of lignin was obtained in CS. This was related to the relaxation of lignin due to breaking of bonds within lignin. The decomposition rates at lignin region were lower in CSC as compared to CS which was related the melting of lignin. The phenomenon of melting and relaxation are closely interlinked. For a bio-material under stresses, the both phenomenon may or may not occur simultaneously. The probability of relaxation is higher than melting during the initial stages of stresses whereas the probability of melting is similar to relaxation at middle stage of annealing. In the final stages of annealing, the melting supersedes relaxation. At the end of annealing, the relaxation may not present at all, and the melting also slows down, and solidification of melted lignin may take place in inner matrix of bio-material.

During the CNSL-extraction some amount of CNSL also remains on the outer surface of CSC as surface oil. This was evident by a broad peak in CSC from 35 to 200 °C centering at 131.6 °C. Thus, this broad peak is ascribed to evaporation of the moisture with surface CNSL in CSC whereas in case of CS, the region from 35 to 200 °C was related to moisture removal. Based on these variations in thermogravimetric signals, it was concluded that CS and CSC were different bio-material.

Residual weight loss data of thermogram (in time domain) of CS and CSC were converted to conversion fraction (α) variation. The decomposition rate *versus* α curve for CS and CSC are given in Fig. 4. Fig. 4 indicated that lignin presence was in the α-span of 0.7–0.9. At 10 °C/min, both the bio-materials were thermally decomposed within 96 min in thermogravimetric analyzer.

3.3. Kinetics

The first-order derivatives of thermogram were analyzed and deconvoluted to obtain the different peaks related to thermal decomposition of hemicellulose, CNSL, cellulose and lignin constituents of both the bio-materials. Linear plot of $\ln(\beta/T^2_{max})$ *versus* $1/T_{max}$ at different heating rates (β) were plotted for CS and CSC to obtain the activation energy and pre-exponential factor related to each deconvoluted peak. Table 3 shows the equation fitted for different peaks obtained for the CS and CSC. The determination of kinetic parameters are erroneous for Peak-1, Peak-2 and Peak-5 in case of CS, and for Peak 5, in case of CSC due to low coefficient of correlation between $\ln(\beta/T^2_{max})$ and $1/T_{max}$. Therefore, the kinetics was not computed for these peaks. To find lignin related activation energy, the KAS method was applied using the iso-conversional lines, and $\ln(\beta/T^2)$ *versus* $1/T$ plots were drawn at α-values of 0.7, 0.8 and 0.9 for CS and CSC as shown in Fig. 5 and Fig. 6, respectively. The overall kinetics were found by using the

Table 3
Kinetic parameters of CS and CSC using peak positions obtained through Gaussian deconvolution.

Peak number	Equation of linear fitting	R^2	Activation Energy (kJ/mole)	Pre-exponential factor, A (min^{-1})
Cashew shell				
Peak-1	$y = 8.8433x - 12.782$	2E-06	–	–
Peak-2	$y = -3824.1x - 6.2346$	0.3334	–	–
Peak-3	$y = -13030x + 8.668$	0.8179	108.34	7.58E + 07
Peak-4	$y = -22235x + 21.978$	0.9786	184.87	7.80E + 13
Peak-5	$y = -6318x - 4.6661$	0.0145	–	–
Cashew shell cake				
Peak-1	$y = -1812.6x - 9.1852$	0.8222	15.07	1.71E + 07
Peak-2	$y = -5923x - 2.3014$	0.88	49.25	5.92E + 04
Peak-3	$y = -10107x + 3.794$	0.8172	84.03	4.49E + 05
Peak-4	$y = -24143x + 25.313$	0.9451	200.74	2.38E + 15
Peak-5	$y = 1789.4x - 15.973$	0.0681	–	–

Where; $y = \ln(\beta/T^2_{max})$ and $x = 1/T_{max}$.

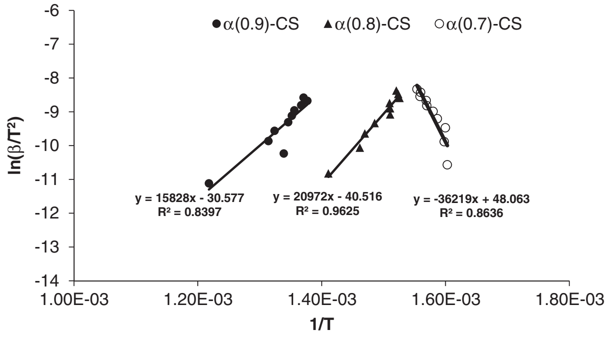

Fig. 5. Determination of kinetic parameters for CS at α-value of 0.7, 0.8 and 0.9.

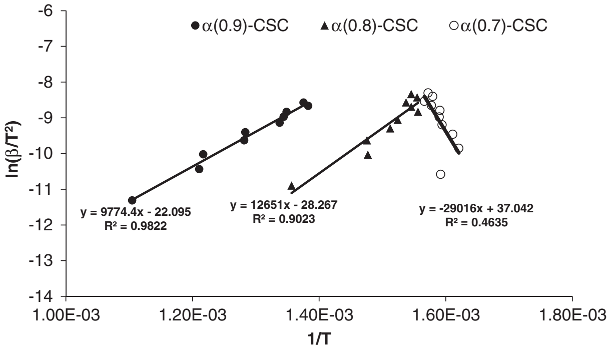

Fig. 6. Determination of kinetic parameters for CSC at α-value of 0.7, 0.8 and 0.9.

KAS method over a complete range of conversion fraction ($\alpha = 0.05$, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85, 0.95). KAS points ($1/T$, $\ln(\beta/T^2)$) were drawn from TGA data at all experimented heating rates (10–100 °C/min) in the α-span of 0.05–0.95 for cashew shell and cashew shell cake. All KAS points are given as Supplementary data. Linear correlation equations of KAS iso-conversional lines ($\ln(\beta/T^2)$ *versus* $1/T$) for CS and CSC are given in Table 4. The coefficient of correlation above 0.8 was considered adequate for comparing the kinetics parameters of both bio-materials. Overall kinetics, activation energies and pre-exponential factors, of thermal degradation of CS and CSC is given in Table 5. The activation energy was found to increase until the lignin region and then activation energy reduced for both bio-materials. The activation energy profile of CS always dominated over the CSC in α-span of 0.05–0.95 indicating that the CS was hard material for thermal degradation. The reduction of activation energy from CS to CSC was highest in lignin related segment (conversion fraction; α-span: 0.70–0.90) showing weakening of lignin. The reductions in values of activation energy from CS to CSC were 61.60, 69.45, 106.61, 50.61 kJ/mole at α-value of 0.7, 0.8, 0.85 and 0.90, respectively.

4. Conclusions

The lignin was prominently noticed in cashew shell as compared to cashew shell cake. The lignin related peak subsided in cashew shell cake. The evidences of surface CNSL were observed in CSC. We established that the CS and CSC are two different bio-materials using thermogravimetric profiling. The activation energies were determined and compared using KAS method for cashew shell and cashew shell cake.

Table 4
Linear correlation equations for KAS iso-conversional lines ($\ln(\beta/T^2)$ *versus* $1/T$) for CS and CSC.

α	Cashew shell		Cashew shell cake	
	Equation of linear fitting for KAS points*	R^2	Equation of linear fitting for KAS points*	R^2
0.05	$y = -12111x + 16.273$	0.5944	$y = -2904x - 2.3365$	0.9019
0.15	$y = -12480x + 14.069$	0.9703	$y = -7331.8x + 4.8852$	0.9468
0.25	$y = -14983x + 17.527$	0.973	$y = -8997.7x + 7.2761$	0.9504
0.35	$y = -18234x + 22.326$	0.9765	$y = -11428x + 10.933$	0.9177
0.45	$y = -21969x + 27.845$	0.9672	$y = -14967x + 16.296$	0.8685
0.55	$y = -28651x + 37.908$	0.9457	$y = -20487x + 24.668$	0.7666
0.65	$y = -32473x + 42.738$	0.9595	$y = -31675x + 41.816$	0.8405
0.75	$y = 14962x - 32.322$	0.1335	$y = 10928x - 26.199$	0.2576
0.85	$y = 23570x - 42.608$	0.9162	$y = 10748x - 24.474$	0.9723
0.95	$y = 9130.7x - 20.517$	0.8857	$y = 9271x - 20.093$	0.9644

Where; $y = \ln(\beta/T^2)$ and $x = 1/T$.

* KAS points ($1/T$, $\ln(\beta/T^2)$) are given as Supplementary data.

Table 5
Kinetics parameters of CS and CSC in α-span of 0.05–0.95.

α	Cashew shell		Cashew shell cake	
	Activation energy (kJ/mole)	Pre-exponential factor (min^{-1})	Activation energy (kJ/mole)	Pre-exponential factor (min^{-1})
0.05	–	–	24.14	3.0E + 04
0.15	103.76	1.6E + 10	60.96	9.7E + 05
0.25	124.58	6.1E + 11	74.81	1.3E + 07
0.35	151.61	9.1E + 13	95.02	6.4E + 08
0.45	182.65	2.7E + 16	124.44	1.8E + 11
0.55	238.22	8.3E + 20	–	–
0.65	267.0	1.2E + 23	264.11	4.6E + 22
0.70	302.85	3.8E + 25	241.25	3.5E + 20
0.75	–	–	–	–
0.80	174.64	8.7E + 21	105.19	2.4E + 16
0.85	195.97	7.5E + 22	89.36	4.6E + 14
0.90	131.88	3.2E + 17	81.27	3.9E + 13
0.95	75.92	7.4E + 12	77.08	4.9E + 12

5. Disclosure

Elemental characterization was obtained (on payment basis) by Central Laboratory, Madhya Pradesh Pollution Control Board, Bhopal, India using AAS.

Acknowledgement

The research work was conducted under the project No. 623 at Central Institute of Agricultural Engineering, Bhopal, India. Directorate of Cashew Research, Puttur, India is acknowledged for supply of raw bio-materials.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2013.12.087.

References

Abdullah, S.S., Yusup, S., Ahmad, M.M., Ramili, A., Ismail, I., 2010. Thermogravimetry study on pyrolysis of various lignocellulosic biomass for potential hydrogen generation. Int. J. Chem. Biol. Eng. 3, 137–141.

Antal, M.J.J., Varhegyi, G., 1995. Cellulose pyrolysis kinetics: the current state of knowledge. Ind. Eng. Chem. Res. 34, 703–717.

Burhenne, L., Messmer, J., Aicher, T., Laborie, M., 2013. The effect of the biomass components lignin, cellulose and hemicellulose on TGA and fixed bed pyrolysis. J. Anal. Appl. Pyrol. 101, 177–184.

Carrier, C., Loppinet-Serani, A., Denux, D., Lasnier, J., Ham-Pichavant, F., Cansell, F., Aymonier, C., 2011. Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass. Biomass Bioenergy 35, 298–307.

Chen, W., Kuo, P., 2011. Isothermal torrefaction kinetics of hemicellulose, cellulose, lignin and xylan using thermogravimetric analysis. Energy 36, 6451–6460.

Ciobanu, C., Ungureanu, M., Ignat, L., Ungureanu, D., Popa, V.I., 2004. Properties of lignin–polyurethane films prepared by casting method. Ind. Crops Prod. 20, 231–241.

Damartzis, T., Vamvuka, D., Sfakiotakis, S., Zabaniotou, A., 2011. Thermal degradation studies and kinetic modeling of cardoon (*Cynara cardunculus*) pyrolysis using thermogravimetric analysis (TGA). Bioresour. Technol. 102, 6230–6238.

Das, P., Gaensh, A., 2003. Bio oil from pyrolysis of cashew nut shell-a near fuel. Biomass Bioenergy 25, 113–117.

Das, P., Sreeletha, T., Gaensh, A., 2004. Bio oil from pyrolysis of cashew nut shell-characterization and related properties. Biomass Bioenergy 27, 265–275.

Doğana, F., Akata, H., Kaya, I., 2008. Synthesis, characterization and thermal degradation kinetics of poly(imino isophthaloyl imino (2,4,8,10-tetraoksoaspiro [5,5] undekan-3,9-dipropylene)). Chin. J. Polym. Sci. 26, 47–53.

Faravelli, T., Frassoldati, A., Migliavacca, G., Ranzi, E., 2010. Detailed kinetic modeling of the thermal degradation of lignins. Biomass Bioenergy 34, 290–301.

Guigo, N., Mija, A., Vincenta, L., Sbirrazzuoli, N., 2009. Molecular mobility and relaxation process of isolated lignin studied by multifrequency calorimetric experiments. Phys. Chem. Chem. Phys. 11, 1227–1236.

Huang, Y.F., Kuan, W.H., Chiueh, P.T., Lo, S.L., 2011. A sequential method to analyze the kinetics of biomass pyrolysis. Bioresour. Technol. 102, 9241–9246.

Kasiraman, G., Nagalingam, B., Balakrishnan, M., 2012. Performance, emission and combustion improvements in a direct injection diesel engine using cashew nut shell oil as fuel with camphor oil blending. Energy 47, 116–124.

Ledakowicz, S., Stolarek, P., 2002. Kinetics of biomass thermal decomposition. Chem. Pap. 56 (6), 378–381.

López-González, D., Fernandez-Lopez, M., Valverde, J.L., Sanchez-Silva, L., 2013. Thermogravimetric–mass spectrometric analysis on combustion of lignocellulosic biomass. Bioresour. Technol. 143, 562–574.

Lu, C., Song, W., Lin, W., 2009. Kinetics of biomass catalytic process. Biotechnol. Adv. 27, 583–587.

Nair, K.P.P., 2010. Cashew Nut (*Anacardium occidentale* L.).The Agronomy and Economy of Important Tree Crops of the Developing World. Elsevier Inc, pp. 21–66 (Print Book ISBN: 9780123846778).

Pandey, M.P., Kim, C.S., 2011. Lignin depolymerization and conversion: a review of thermochemical methods. Chem. Eng. Technol. 34, 29–41.

Patel, R.N., Bandyopadhyay, S., Ganesh, A., 2006. Extraction of cashew (*Anacardium occidentale*) nut shell liquid using supercritical carbon dioxide. Bioresour. Technol. 97, 847–853.

Sait, H.H., Hussain, A., Salema, A.A., Ani, F.N., 2012. Pyrolysis and combustion kinetics of date palm biomass using thermogravimetric analysis. Bioresour. Technol. 118, 382–389.

Sbirrazzuoli, N., Vincent, L., Mija, A., Guigo, N., 2009. Integral, differential and advanced isoconversional methods complex mechanisms and isothermal predicted conversion–time curves. Chemom. Intell. Lab. Syst. 96, 219–226.

Shen, D.K., Gu, S., Bridgwater, A.V., 2010. The thermal performance of the polysaccharides extracted from hardwood: cellulose and hemicellulose. Carbohydr. Polym. 82, 39–45.

Shukla, R., Agarwal, P., Kumar, A., 2010. Crystallization kinetics in glassy Se_{100-x} In_x systems using iso-conversional methods. Chalcogenide Lett. 7, 249–255.

Singh, R., Jena, U., Patel, J.B., Sharma, A.M., 2006. Feasibility study of cashew nut shells as an open core gasifier feedstock. Renewable Energy 31, 481–487.

Tippayawong, N., Chaichana, N., Promwangkwa, A., Rerkkriangkrai, A., 2011. Gasification of cashew nut shells for thermal application in local food processing factory. Energy Sustainable Dev. 15, 69–72.

Tsamba, A.J., Yang, W., Blasiak, W., 2006. Pyrolysis characteristics and global kinetics of coconut and cashew nut shells. Fuel Process. Technol. 87, 523–530.

Tsamba, A.J., Yang, W., Blasiak, W., Wójtowicz, M.A., 2007. Cashew nut shells pyrolysis: individual gas evolution rates and yields. Energy Fuels 21, 2357–2362.

Vasile, C., Popescu, C., Popscu, M., Brebu, M., Willfor, S., 2011. Thermal behavior/treatment of some vegetable residues. IV. Thermal decomposition of eucalyptus wood. Cellul. Chem. Technol. 45, 29–42.

Wang, Q., Zhao, W., Liu, H., Jia, C., Xu, H., 2012. Reactivity and kinetic analysis of biomass during combustion. Energy Procedia. 17, 869–875.

White, J.E., Catallo, W.J., Legendre, B.L., 2011. Biomass pyrolysis kinetics: a comparative critical review with relevant agricultural residue case studies. J. Anal. Appl. Pyrol. 91, 1–33.

Yuliana, M., Huynha, L., Hob, Q.P., Truongb, C., Ju, Y., 2012. Defatted cashew nut shell starch as renewable polymeric material: isolation and characterization. Carbohydr. Polym. 87, 2576–2581.